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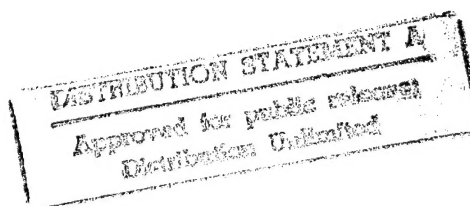
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AIR OXIDATION OF URANOUS SOLUTIONS

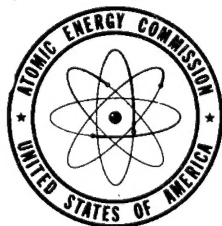
By  
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December 21, 1950

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TOPICAL REPORT MITG-261

AIR OXIDATION OF URANOUS SOLUTIONS

By

James H. Pannell

A B S T R A C T

Rates of oxidation of U(IV) solutions by air under various conditions similar to those prevailing in ore leach liquors were determined.

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Approved for A. M. Gaudin, Director

By

*A. W. Owens*

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December 21 1950

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TOPICAL REPORT MITG-261AIR OXIDATION OF URANOUS SOLUTIONS

By

James H. Pannell

I. INTRODUCTION

The oxidation of uranous solutions by air has been studied at the University of California, Radiation Laboratory<sup>1/</sup>, and briefly by chemists<sup>2/</sup> interested in the titrimetric determination of uranium but seems to have received less attention by those concerned with the extraction of uranium from ores. This is in spite of the development of methods for separating uranium by precipitation of a uranous phosphate after reduction of U(VI) to U(IV) in leach liquors, as practiced on Rand ores by GML and MIT (e.g. MITG-A85, -A90, -A92, -A99, and -A103) on phosphate ores by BMI and MIT (MITG-250) and on shales by Y-12 (Y-464). Moreover, economic considerations preclude the possibility of preventing re-oxidation by maintenance of a very low pH as is done in analytical work. It was in connection with a systematic study of uranous phosphate (MITG-245) that tests were begun to determine roughly the rate of oxidation of uranous solutions by air. Completion of the phosphate investigation presented an opportunity for a more intensive study of this oxidation phenomenon.

The uranium (IV-VI) oxidation-reduction potential of  $-0.33^*$  volts<sup>3/</sup> shows that uranous solutions are fairly strong reducing agents; moreover the pronounced tendency for uranyl ion to form soluble complexes indicates that this potential will be less negative in many actual solutions.

The concentration of oxygen in air-saturated water at 25°C and 760 mm Hg is 5.78 ml per liter or 0.26 millimolar (for O<sub>2</sub>). An equivalent concentration (0.52 mM) of uranium would be represented by 0.12 g U/l or 0.14 g U<sub>3</sub>O<sub>8</sub>/l. If one assumes a similar solubility for air in ore leaching solution containing 0.4 g U/l, it is equivalent to about one third of the uranium extracted. Thus one can realize that the amount of air which will dissolve in the solution is significant for the uranium concentration encountered in leaching low-grade ores.

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\*American System.

## II. SUMMARY

The air oxidation of uranous solutions occurs at rates dependent on the type of acid used and its pH, the concentration of uranium, the presence or absence of catalytic ions, viz. silicate, molybdenum, copper or cobalt, and the ionic strength of the solution. Some of the factors are interdependent, for instance, in  $\text{H}_2\text{SO}_4$  less uranium was oxidized at the higher concentrations while in  $\text{HCl}$  the reverse was true.

Most of the tests were carried out at pH 1.0 in order to obtain conditions similar to those in leach liquors.

Application of the results to leach solutions suggests that air saturation at pH 1.0 might oxidize between 0.2 and 1.5 g U/l per hour; that silicate might catalyze the oxidation; and that salts will hinder it.

### III. EXPERIMENTAL PROCEDURE AND RESULTS

Aeration was performed by rapidly passing air through a fritted glass disc near the bottom of a 250-ml gas washing bottle. Bottles were connected in parallel, for multiple aerations, in order to have the same air pressure in each. The extent of oxidation was determined periodically by removal of 10 or 25-ml samples, addition of  $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ , and their titration with cerate solutions using ortho-phenanthroline as an indicator. Titration readings were converted to uranium concentration, in millimoles per liter, and are reported in that form.

Most experiments were carried out at room temperature which, unfortunately, was not always steady, but some were later made in a thermostated water bath.

After a few exploratory tests had shown that uranous solutions at pH about 1.0 were oxidized by air at measurable rates, tests were run to determine the effects of varying (a) the pH, (b) the acid, (c) the concentration of uranium, (d) the presence of other cations, and (e) ionic strength.

#### The Effect of pH and Acid Type

As the uranyl ion is an oxy-ion while the uranous ion is not, the conversion of one to the other should involve a change of free energy which is dependent on pH to a marked extent. There is ample confirmation for this surmise e.g. in the effect of pH on oxidation-reduction potential. As would be expected, the oxidation of uranous solutions was found to be considerably more rapid at pH 1.5 than at pH 1.0 and differences in pH of 0.1 are, therefore, of some significance. These readings, made on a Beckman Model H-2 pH meter using a glass electrode, calibrated at pH 1.0 or 2.0 with Clark and Lubs buffer mixtures, are probably within 0.05 of the correct figure at pH above 1.0 and within 0.1 at lower pH.

The experimental procedure comprised reduction of a uranyl solution, pH about 0.8, by a Jones reductor, whereafter dilution was made to pH 1.5. Aliquots of the solution were then acidified to various degrees and placed in gas washing bottles for aeration. Initial samples were taken from each bottle and titrated with cerate; others were taken after various periods of aeration. In this manner, the comparative effect of pH could be determined as all solutions in each test were of the same initial concentration and at the same temperature. Observations of this effect are depicted by the curves in Figures 1, 2 and 3, where concentration of U(IV) oxidized, in g/l is plotted versus hours of aeration for sulfuric, hydrochloric and perchloric acids. The initial concentration of U(IV) in the sulfuric acid solutions was about 11 millimolar; in hydrochloric, 26 mM; and in perchloric, 25 mM. During the second hour, the amounts of uranium oxidized at the four acidities of  $\text{H}_2\text{SO}_4$  were as follows:

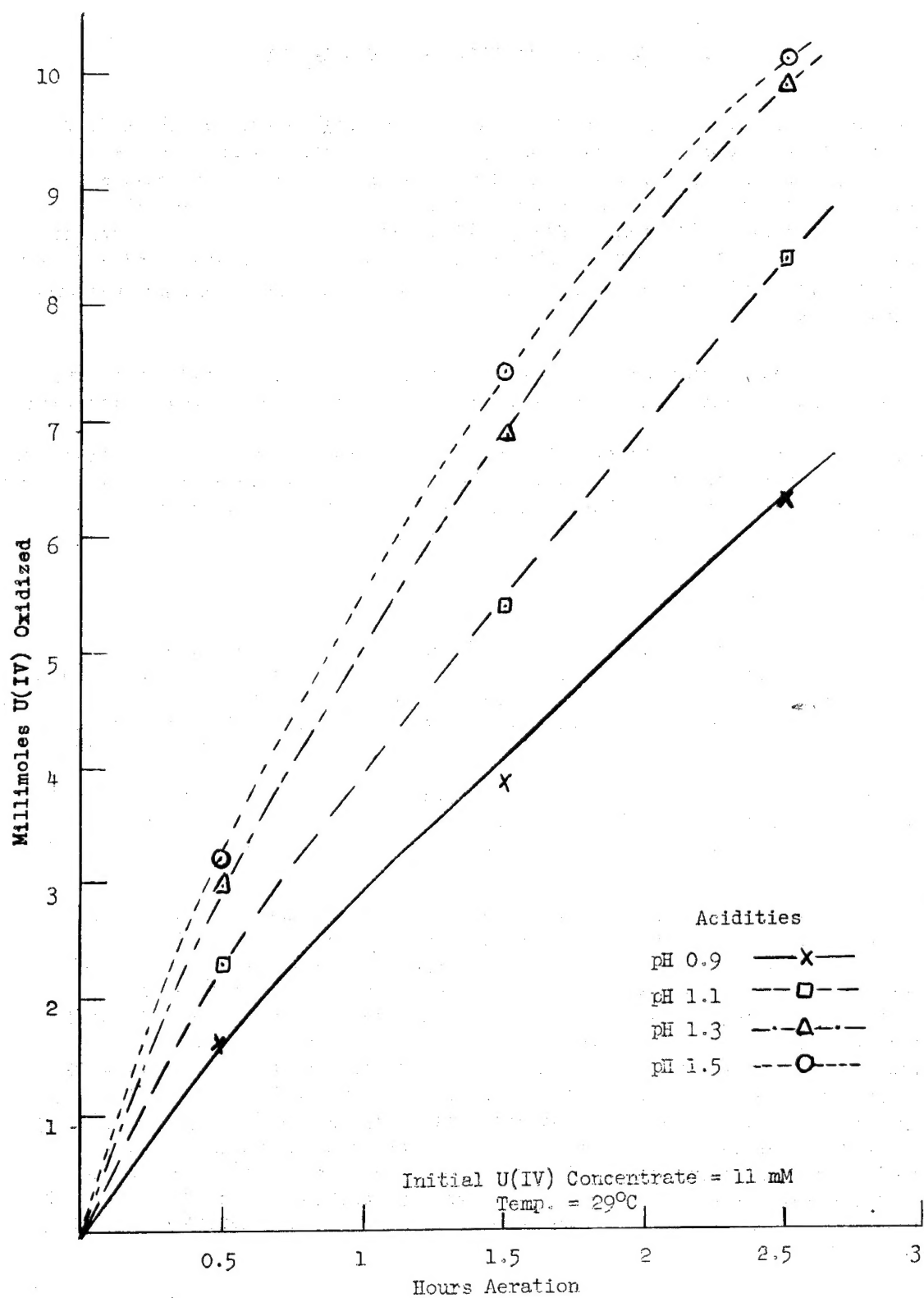


Figure 1. Effect of pH on Air Oxidation of Uranous Sulfate



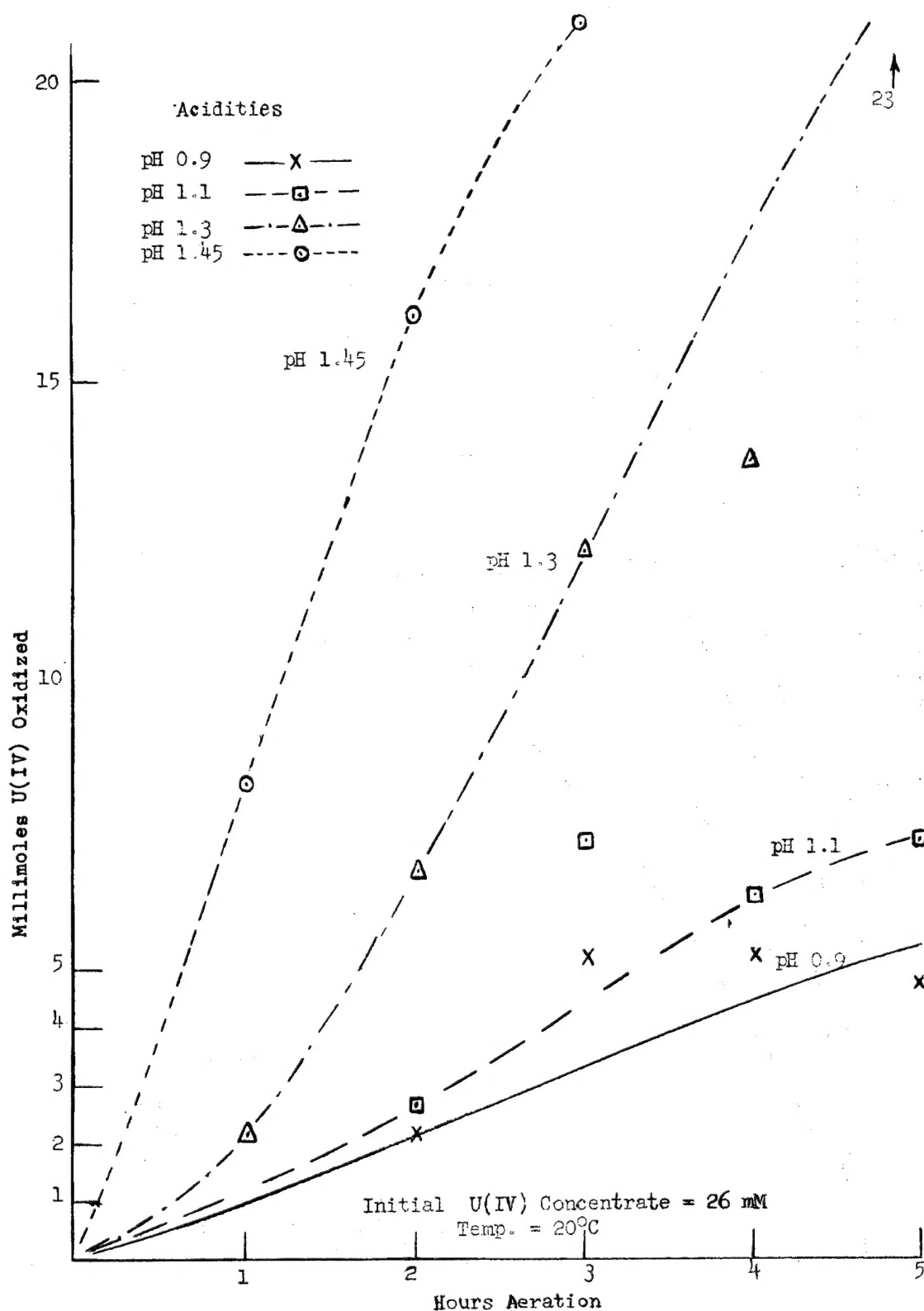


Figure 2. Effect of pH on Air Oxidation of Uranous Chloride

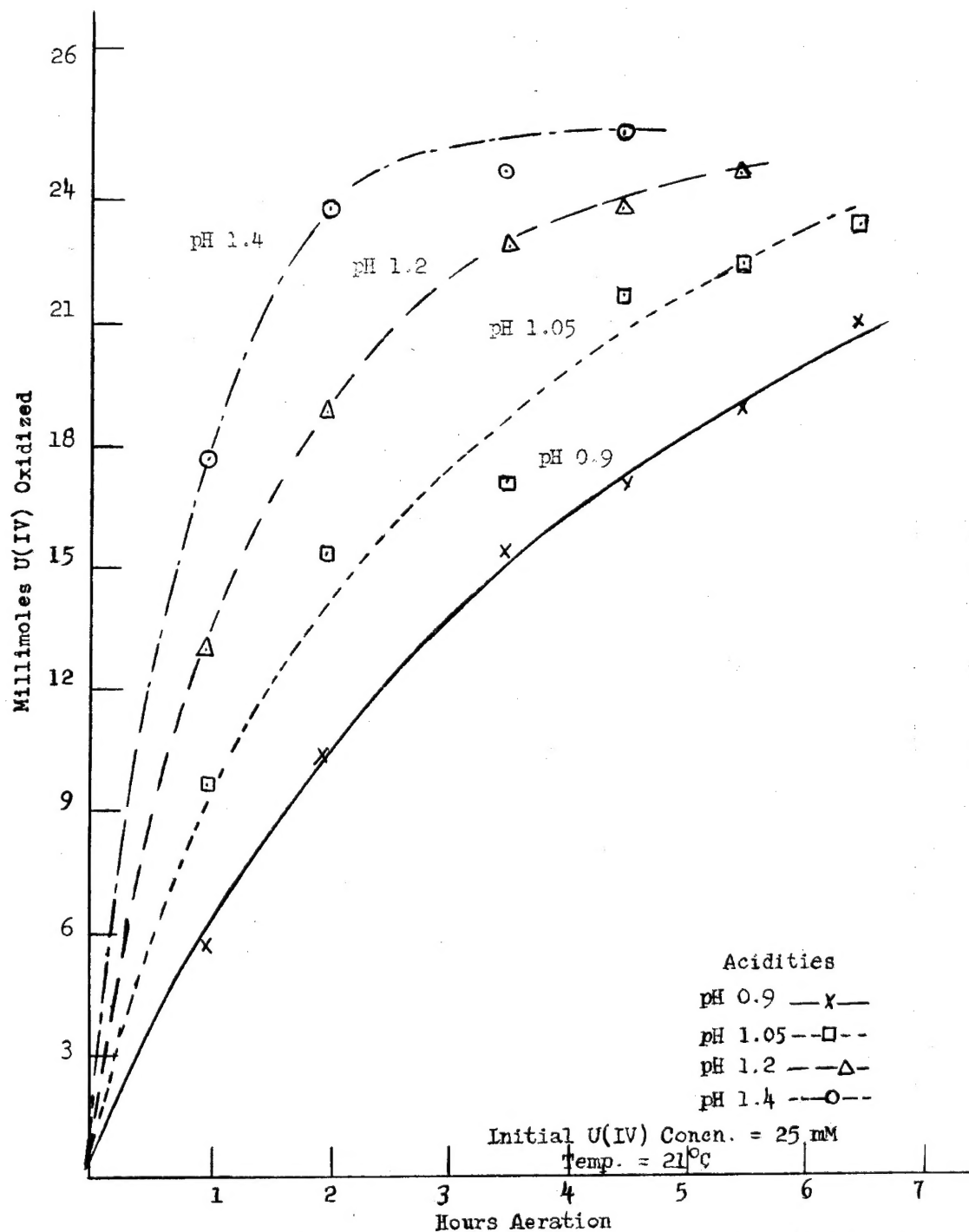
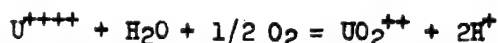


Figure 3. Effect of pH on Air Oxidation of Uranous Perchlorate

<u>pH</u>	<u>mM U(IV)/l Oxidized</u>
0.9	2.3
1.1	3.0
1.3	3.6
1.5	3.4

whence it can be seen that the rate of oxidation in sulfuric acid increased approximately as the inverse square root of the hydrogen ion activity. This is a lower order dependence on pH than would have been predicted from the reaction



In hydrochloric acid, pH readings were made before and after oxidation and a mean value obtained. Rates of oxidation during the second hour, as shown by Figure 2, were as follows:

<u>pH</u>	<u>mM U(IV)/l Oxidized</u>
0.9	1.0
1.1	1.5
1.3	4.5
1.45	8.0

and show a considerably greater dependence on pH than do those obtained for sulfuric acid. Between pH 1.0 and 1.45, the dependence is roughly on the square of the hydrogen ion concentration.

In perchloric acid, the pH effect is again smaller than would be anticipated but as the curves shown in Figure 3 are far from straight lines, it is difficult to compare their slopes. During the first hour, the amounts of uranium oxidized were as follows:

<u>pH</u>	<u>mM U(IV)/l Oxidized</u>
0.9	5.5
1.05	9.3
1.2	12.7
1.4	17.3

and these data give a straight-line relationship with a slope of about eight millimoles of U(IV) per 0.3 pH units.

At pH 1.0 the relative rates of oxidation in perchloric, sulfuric and hydrochloric acids were 8, 2-1/2 and 1 respectively. This is in qualitative agreement with earlier results<sup>1</sup> in which it was postulated that chloride ion and, to a lesser extent, sulfate ion, inhibited the reaction.

#### The Effect of Uranium Concentration

The highest rate of oxidation so far considered was about 17 mM per hour which is equivalent to some 33 times the saturation concentration of oxygen. Therefore, the oxygen turnover time was 2 minutes or the rate of oxygen input at least 0.16 mM per minute. Figures derived from the curves in Figure 3 give no

evidence that the limit in the rate of oxygenation was being approached so it is safe to assume that in all solutions the concentration of oxygen was constant. The rate of oxidation, then, should be proportional to the amount of uranium present and the curves should have the exponential shape characteristic of a first order reaction. Those in Figure 3 appear to do so.

A direct determination of the effect of concentration was made first on sulfuric acid solutions, at pH 1.0 with initial uranium concentrations of about 300, 90, 30, 10 and 5 mM. The remarkable results obtained indicated much faster rates of oxidation in the more dilute solutions; in fact, practically no oxidation took place in the two most concentrated solutions. Similar tests were made in hydrochloric and perchloric acids but these gave results in better agreement with the kinetic theory outlined in the previous paragraph. Repetitions of the test in sulfuric acid were made with careful measurement of pH before and after aeration but the results were substantially the same as those obtained previously and one set is plotted in Figure 4. Initial U(IV) concentrations were 36, 18, and 8 mM.

Results obtained for hydrochloric acid and initial U(IV) concentrations of 18, 10, 5 and 2 mM are shown in Figure 5. In each solution slightly less than 40 per cent of the uranium was oxidized in 7 hours and during this period one may say that the rate was proportional to U(IV) concentration although no curvature of the lines is apparent. Hence, the constant in the equation

$$\frac{d \text{ U(IV)}}{dt} = -k [\text{U(IV)}]$$

may be calculated. This was done by drawing ordinates, Figure 5, to points on the line representing 25 per cent oxidation and averaging the resultant times to give 4.1 hours. Then the ratios of initial to 4.1 hour concentrations were 4:3 so that

$$k = 1/4.1 \times \ln 4/3$$

giving  $k = 0.0695 \text{ hr}^{-1}$  and half-life,  $t_{1/2}$ , of 10 hours. It is not postulated that this rate constant can be applied at very much higher concentrations of uranium where the reaction is unlikely to have first-order characteristics. Parenthetically it may be noted that leach liquors are about 1 mM in uranium.

#### The Effect of Some Other Cations

As the oxidation of U(IV) ions is not likely to be a simple one-step reaction it is possible for other cations to catalyze intermediate steps. Those cations occurring in leach liquors in appreciable concentration are  $\text{Fe}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Al}^{+++}$  and  $\text{Mn}^{++}$ . The present study included also silicate, copper, cobalt, molybdenum and vanadium.

French workers<sup>4/</sup> have already reported a catalytic oxidation caused by copper and molybdenum, while an earlier report<sup>5/</sup> of catalysis by copper alone was made. It was found, in this work that cobalt, copper, molybdenum and silicate, in decreasing effectiveness, were capable of increasing the rate of oxidation.

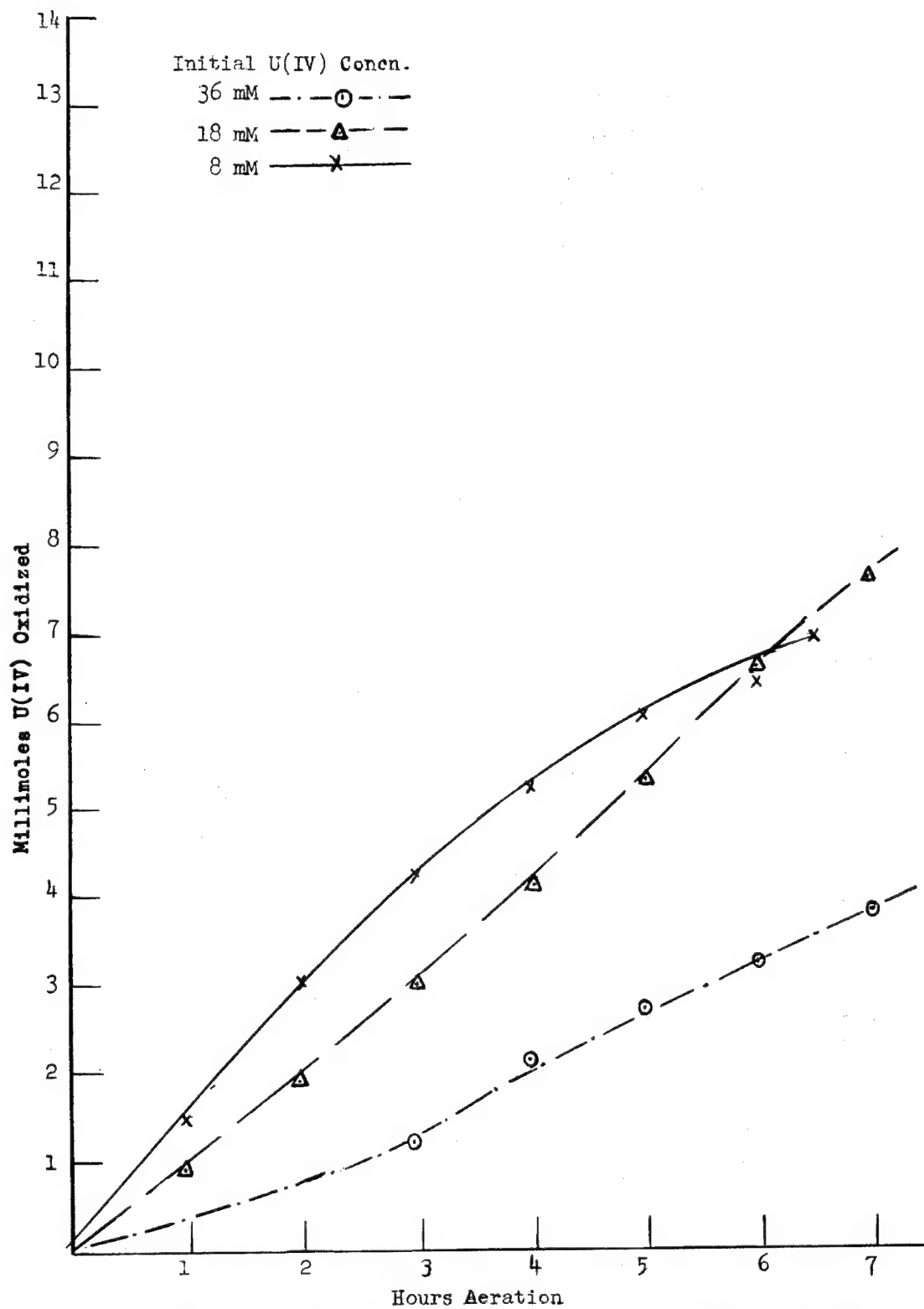


Figure 4. Effect of U Concentration on Rate of Air Oxidation in pH 1.0  $\text{H}_2\text{SO}_4$

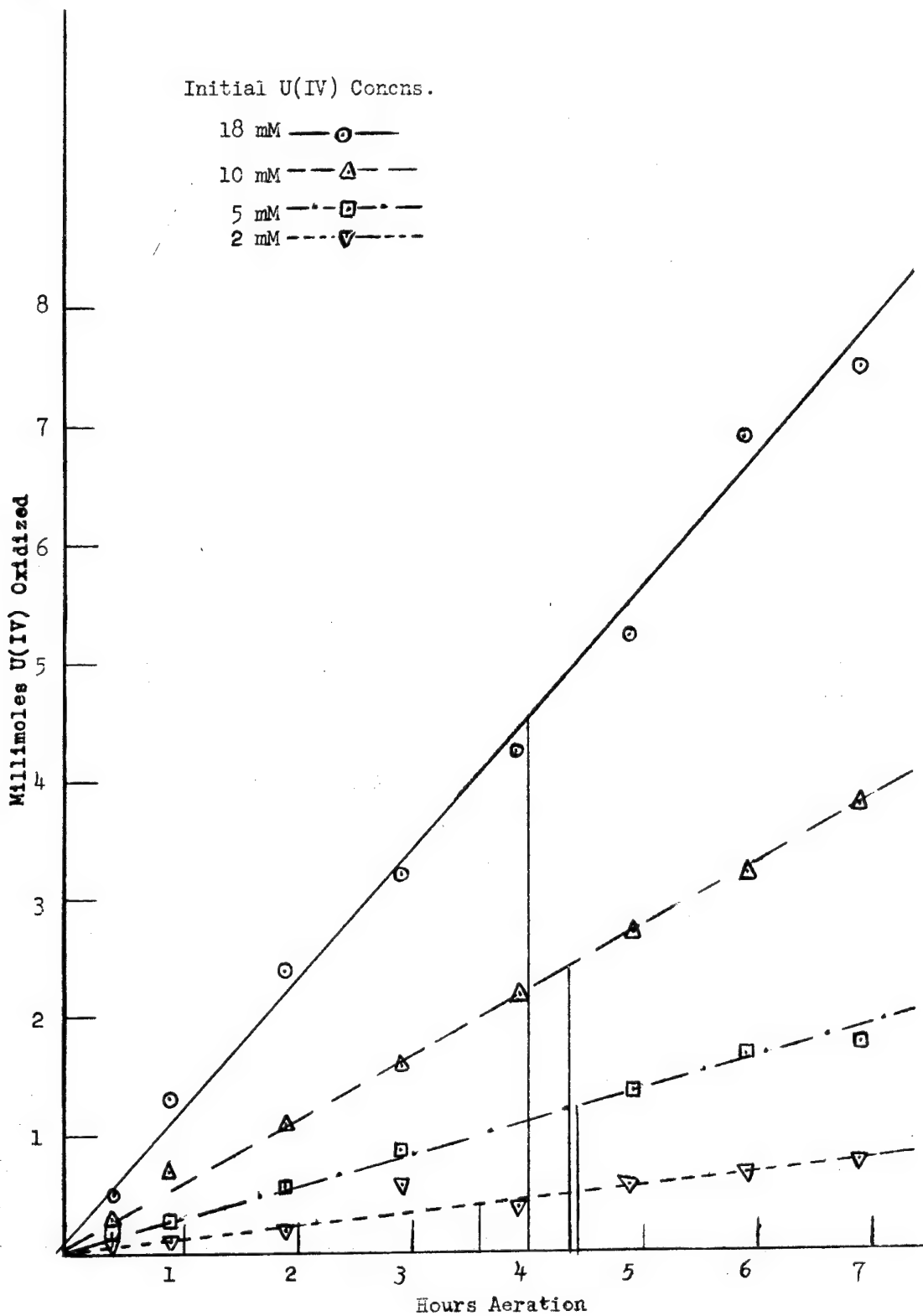


Figure 5. Effect of U Concentration on Rate of Air Oxidation at pH 1.0 in HCl

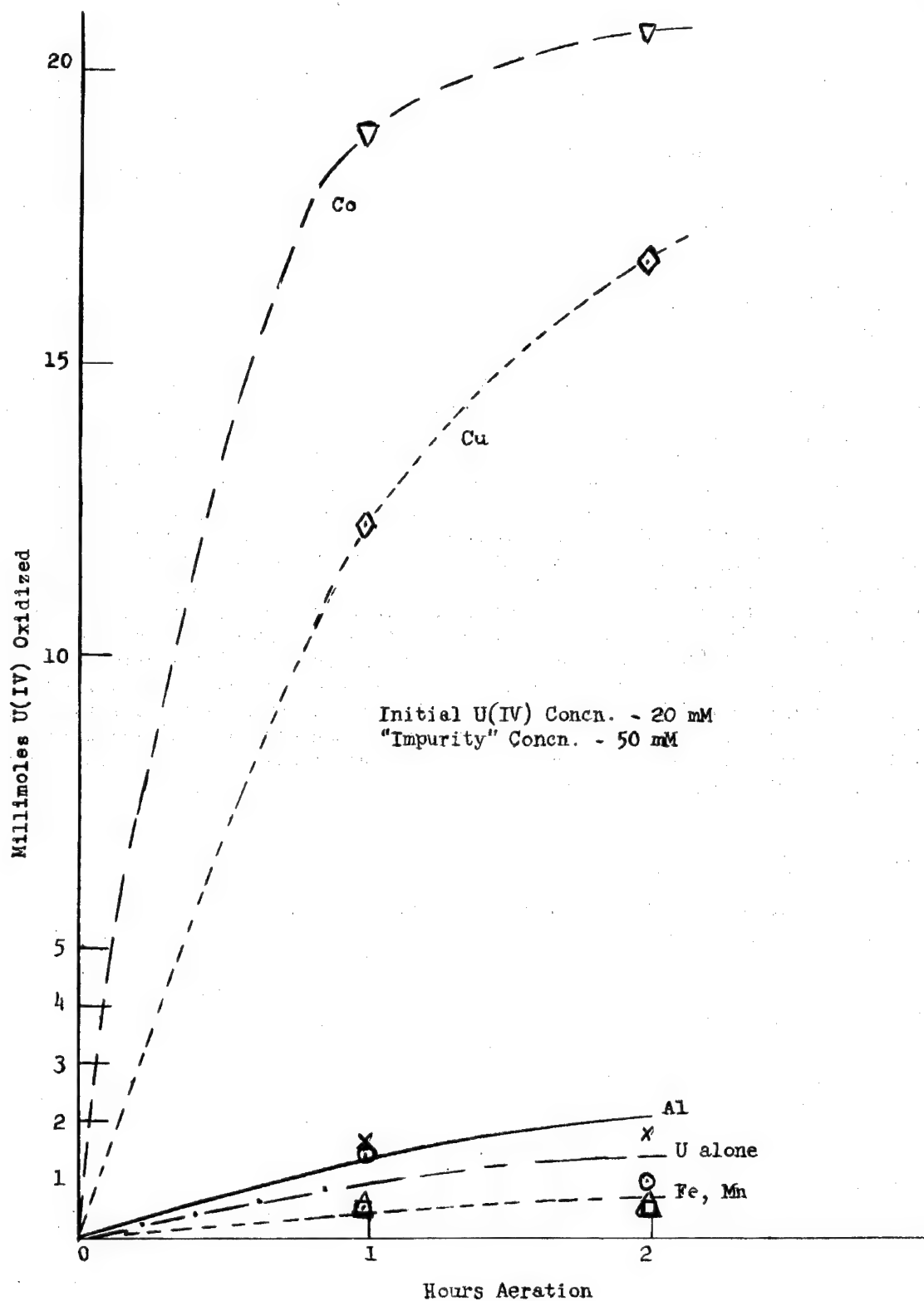


Figure 6. Catalytic Effect of Co and Cu on Air Oxidation of U(IV) in pH 1.0  $\text{H}_2\text{SO}_4$

The experimental procedure consisted of reducing the uranium in  $\text{H}_2\text{SO}_4$  as before, adjusting the pH to 1.0, dividing the solution into a number of parts, adding solutions at pH 1.0 of the reduced ions under investigation and keeping one part for control. Molybdenum sulfate was prepared by acidification of ammonium molybdate solution, reduction with  $\text{SO}_2$  and removal of excess  $\text{SO}_2$ . Other solutions were prepared directly from the sulfate except  $\text{H}_2\text{SiO}_3$  which was formed by acidification of sodium metasilicate.

The results of a comparative test are shown in Figure 6 for concentrations 20 millimolar in uranium and 50 millimolar in copper, cobalt, aluminum, iron or manganese.

Cobalt and copper appeared to be effective catalysts so they were included in a second test together with silicate and molybdenum. The first three ions were tested at two concentrations, 10 and 20 millimolar; precipitation of some  $\text{MoO}_3$  during preparation of the molybdenum solution reduced its concentration to, perhaps, 5 millimolar. The results of this test are shown in Figure 7 where it can be seen that molybdenum, copper and cobalt approximately doubled the rate of oxidation of uranium. Unfortunately for quantitative deduction, the solution containing uranium alone exhibited a much higher rate of oxidation than was anticipated. The possibility that vanadium might catalyze the oxidation was checked by an experiment with solutions of uranous sulfate, uranous plus vanadous (III) sulfates and vanadous sulfate. Aeration of the three, all at pH 1.3, at  $23^\circ\text{C}$  showed that in some four hours very little oxidation occurred in the uranous solution, about six millimoles of vanadium (III) were oxidized in the pure  $\text{V}_2(\text{SO}_4)_3$  solution and four milliequivalents (or 2 mM) were oxidized in the mixed solution. It is therefore apparent that (a) vanadium (III) is oxidized faster than uranium (IV) and (b) vanadium does not accelerate the rate of oxidation of uranium.

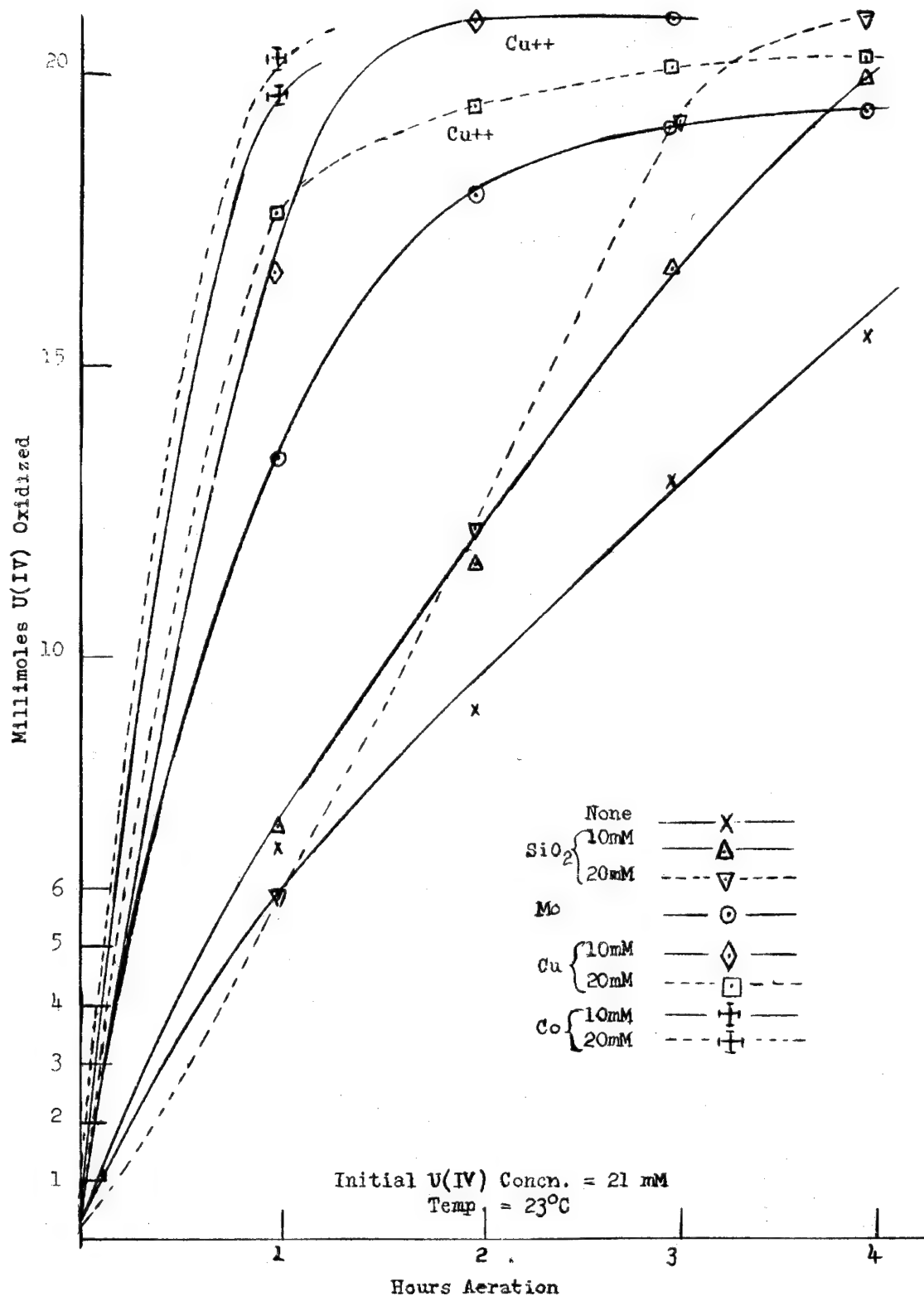
#### Effect of Ionic Strength

Aqueous solutions of  $\text{U(IV)}$  are known to contain the tetrapositive ion -- the highest charge exhibited by any cation -- and one should, therefore, expect ionic strength to have a profound effect on its reactions. For instance, Bjerrum has shown that the reaction rate,  $k$ , at ionic strength  $\mu$ , between ions of charge  $Z_A$  and  $Z_B$  is

$$\log_{10} \frac{k}{k_0} = 2CZ_AZ_B\sqrt{\mu}$$

where  $k_0$  is the true reaction rate constant,  $C$  the Debye-Huckel constant and  $Z_AZ_B$  the product of the ionic charges. Thus for a hypothetical reaction between  $\text{U}^{4+}$  and  $\text{O}^{2-}$ , where  $Z_AZ_B = -8$ ,  $k$  should vary as  $e^{160\sqrt{\mu}}$  and, consequently, fall rapidly with increasing ionic strength. An additional effect of ionic strength, however, is to decrease the solubility of oxygen so the observed effect may be due to either or both factors. Addition of potassium sulfate to a solution of  $\text{U(IV)}$  in sulfuric acid caused precipitation of much of the uranium so the experiment was confined to HCl. Each of five solutions contained 13 mM of  $\text{U(IV)}$  as chloride in pH 1.0 HCl giving a  $\mu$  of 0.15. Additions of KCl were made to increase the ionic strengths to 3.2, 2.2, 1.2, 0.6 and 0.4. The results of aerating the solutions are shown in Figure 8. As the test was made under ambient conditions, the effect of a  $5^\circ\text{C}$  rise in air temperature toward the end



Figure 7. Catalytic Effect of SiO<sub>2</sub>, Mo, Cu and Co

Ionic Strengths  
0.40 — x —  
0.65 — Δ —  
1.2 — — —  
2.2 — □ —  
3.2 — ◇ —

Initial U(IV) Concentrate 14 mM

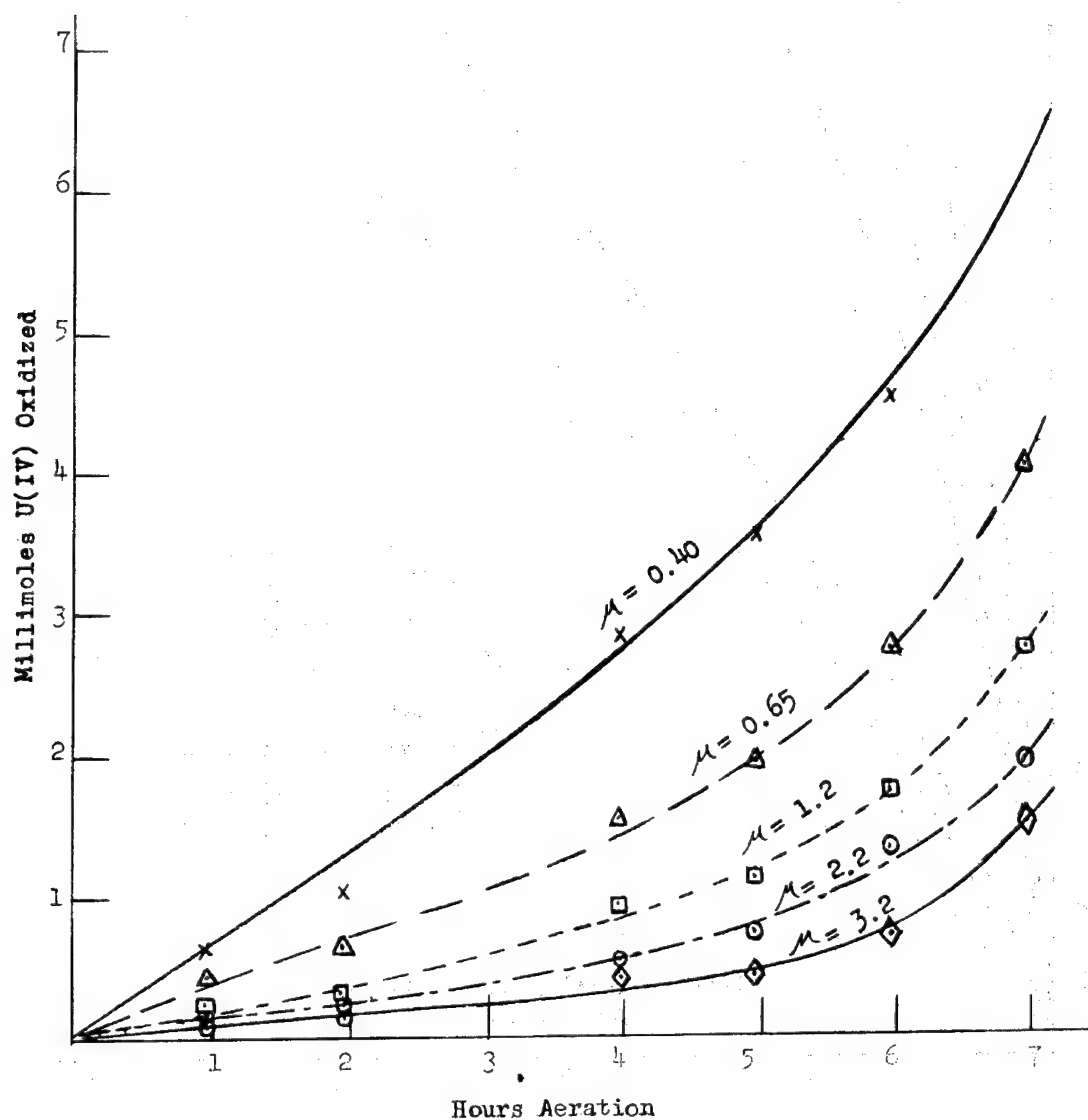


Figure 8. Effect of Ionic Strength on Rate of Oxidation in pH 1.0 HCl

of the test caused an upward curvature in the lines. The conclusion from this test is that increases in ionic strength cause decreases in the rate of oxidation of U(IV) by air. Insufficient work was done to show how the effect is produced but some deductions may be made on the basis of published data<sup>5</sup> regarding the salting out of oxygen where a salting coefficient,  $k_m$ , of about 0.11 is found for KCl. Insertion in the equation

$$\ln \gamma_{(s)} = k_m \mu$$

where  $\gamma_{(s)}$  is the activity coefficient of oxygen in the salt solution, produces results tabulated below:

$\mu =$	0	0.4	0.65	1.2	2.2	3.2
$\gamma_{(s)} =$	1.0	1.6	2.0	3.7	10	23

Although it would be naive to accept the values for  $\gamma_{(s)}$  calculated for solutions of high  $\mu$  at their face value, they are probably a useful guide in pointing out the extent to which oxygen was salted out of the solutions.

#### Comparative Test with Leach Solution

An experiment designed to compare the behavior of uranium in pure solution with that in a leach liquor was made by aeration of a pure uranous sulfate solution and a solution composed 80 per cent of Y-type leach liquor. Both contained 34 mM U(IV) and were aerated at pH 1.0 and at 30°C. The results, plotted in Figure 9, suggest that there is very little difference between the effects of the two media on the rate of oxidation.

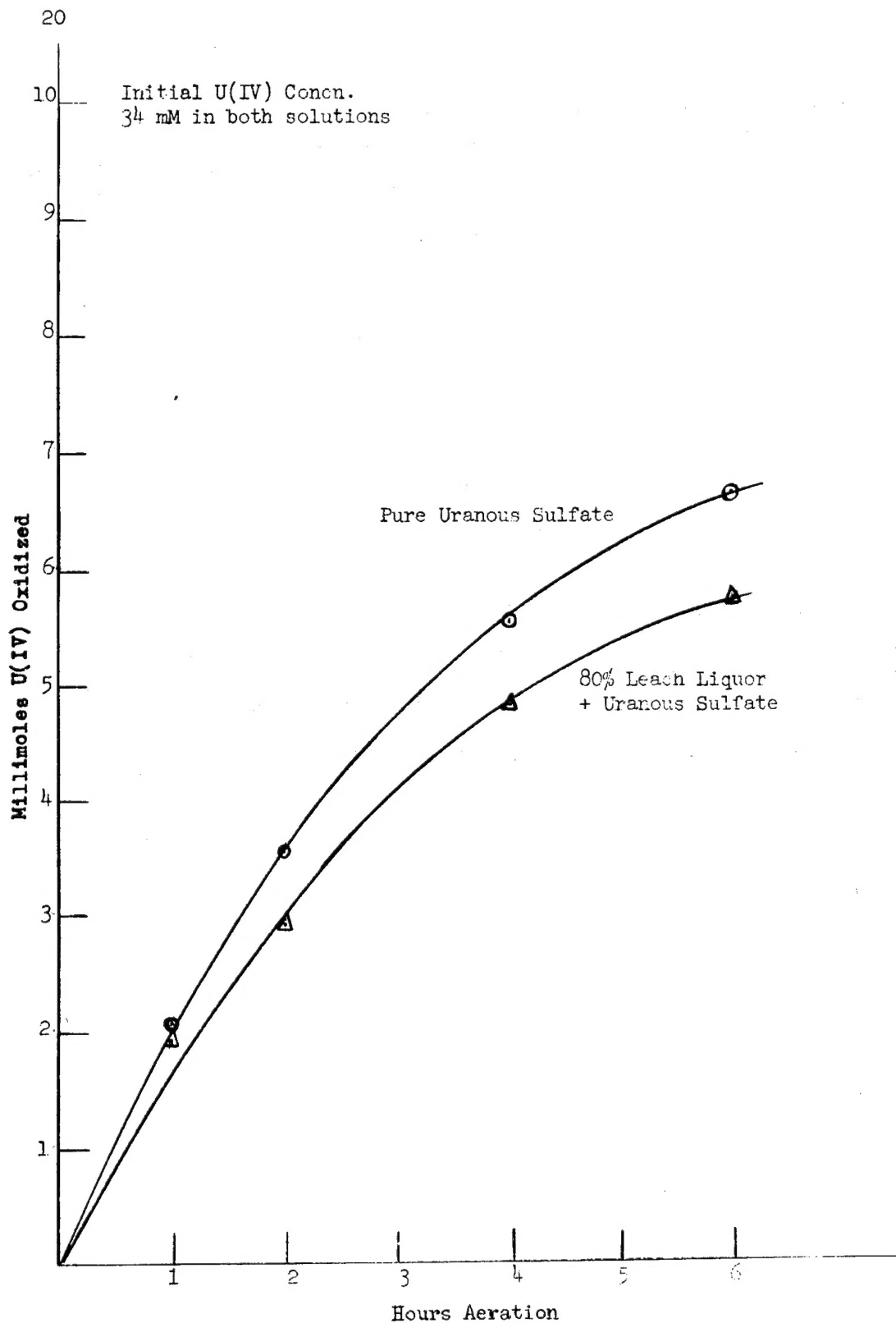


Figure 9. Comparison of a Leach Liquor, Spiked with U(IV), with a Pure Solution

#### IV. CONCLUSIONS

The experimental results given in the preceding pages are important in uranium hydrometallurgy if reduction of uranium is necessary. As it may not be economically feasible to maintain a pH as low as about 0.5, reduction of the uranium will not be rapid and its reoxidation by air should be anticipated.

It is probable that the uranium in a reduced leach solution from Rand ore is oxidized about as fast as when in a pure solution at the same pH.

Maintenance of as low a pH as possible and exclusion of air and of copper, cobalt and molybdenum are conducive to the preservation of uranium in a reduced state.

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